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The Colorimetric Determination of "Porphyroxine Meconidine" The Relation between Tintometer and Spectrophotometric Measurements obtained in the Determination of "Porphyroxine-Meconidine" in Opiums

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In continuation of the international programme of scientific research undertaken pursuant to resolutions 159 II C (VII) and 246 F (IX) adopted by the Economic and Social Council on 3 August 1948 and 6 July 1949, respectively, the Secretary-General is presenting the following paper contributed by Canadian scientists.

The work reported here is a continuation of the narcotics research programme of the Canadian Government. The spectrophotometric data presented here were obtained along with the Lovibond tintometer readings previously reported in document E/CN.7/207, 19 October 1950. The present paper establishes a relation between the tintometer readings and the spectrophotometric readings. The measurement of the "porphyroxine-meconidine" colour is of importance to the determination of origin of seized opium.

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THE RELATION BETWEEN TINTOMETER AND SPECTROPHOTOMETRIC MEASUREMENTS OBTAINED IN THE DETERMINATION OF "PORPHYROXINE-MECONIDINE" IN OPIUMS

by

Charles G. Farmilo and P.M.L. Kennett

I. Purpose of the Paper

1. The purpose of the present paper is to show the relation between tintometer and spectrophotometer measurements, both used to express the relative concentrations of "porphyroxine-meconidine" from one gramme samples of opium. "Porphyroxine-meconidine" is determined indirectly by measuring the relative colour concentration of the red coloured material (porphyr) obtained by the treatment of "porphyroxine-meconidine" with acid. The tintometer and spectrophotometric measurements are expressed as red units and absorbances respectively. The object of the paper is to show that a Lovibond red unit is equivalent to a definite fraction of an absorbance unit. This paper will enable chemists in other laboratories to interpret Lovibond data obtained in this series, E/CN.7/195, E/CN.7/207 and ST/SOA/SER.K/4, in terms of absorbances (optical densities) obtained at definite wave lengths of light. The samples of opium used in this study were obtained in the same way as those used previously, Farmilo and Kennett (20).

II. Experimental Procedures

2. Preparation of "Porphyroxine-meconidine" for Spectrometry:

The determination of "porphyroxine-meconidine" was carried out according to the method described by United Nations chemists, (See document E/CN.7/195). Opium (1.5 gm) was prepared and diluted to 60 ml. of which an aliquot (40 ml) was taken for ether extraction (representing one gramme of the original opium) and separation of ether-soluble alkaloids, including the "porphyroxine-meconidine". The "porphyroxine-meconidine" in the dried residue was then transformed into porphyr hydrochloride by treatment with 5 ml of 1% v/v HCl solution (1 cc concentrated HCl/100 cc water). The red coloured solution of porphyr hydrochloride was accurately diluted to 10 ml in a volumetric flask. A portion of this red solution (about 0.7 ml) was used for tintometer measurement

employing a 1/16 inch cell. Measurements published by the United Nations chemists were obtained in a 1/8 inch cell and our readings as given in the present paper should be multiplied by two, to compare with their data (17) and (18), and with the data used by Fuchs and Ullrich (9). (In E/CN.7/207 the multiplication by two was made in reporting the results (20).) For spectrometric measurements 1.5 ml of the above red solution was diluted to 25 ml in a volumetric flask. The concentration of these solutions in terms of the original weight of opium (1 gm in a 40 ml aliquot) was the same for all samples, equivalent to (0.1 x 1.5 x 4) = 0.6 gm opium per 100 ml aqueous HCl solution.

3. Instrumental Techniques Employed:

It is not proposed to describe in detail methods for determining absorption spectra, since these have been dealt with by many workers, Brode (1), Harrison and Loofburrow (2), Dufrasne (3), Friedel and Orchin (4), Twyman and Lothian (5), Mellon (14), and others (12). Hirt's "Sources of information on absorption spectrophotometry" lists the most up-to-date references, books, review articles, collections of data, etc., on the subject (21). The usual precautions were taken against solvent impurities, instrumental aberrations and in the use of the cells.

Comparison of Absorbance Curves Measured on Different Spectrophotometers:

4. Absorbances were measured in comparison with tintometer readings on three different spectrophotometers:

(1) A Coleman Universal Spectrophotometer, Model 11, using a glass filter No. PC.4(11-214) with an optimum transmittance range from 400 to 650 mμ and a band width about 35 mμ at 511 mμ.

(2) A Beckman Model B Spectrophotometer which is described in detail elsewhere (6) was used. The Beckman B wave length range is 320-1000 mμ with band width about 4 mμ at 520 mμ. The instrument is a rapid accurate device for routine photometric and spectrometric analyses. The model B uses a Fery prism for the light dispersion element, a new type wave length control mechanism and a new reed suspension continuously variable slit mechanism for controlling band width.

(3) A Beckman DU quartz spectrophotometer which has a range from 210-1000 mμ and an effective band width at 520 mμ equal to 2 mμ using a slit width 0.1 mm. A description of the latest model has been given recently (6).

5. Absorbances measured by means of the three spectrophotometers referred to above are plotted against wave length in Figure 3. Curves (2) and (3) in Figure 3 were obtained using a red solution prepared from a sample of Indian opium (No. 6, Situ Mau Province) using Coleman and Beckman B instruments respectively. Curve (1) was plotted from absorbances used in constructing curve (3), making allowance for difference in cell diameter (corresponding to a 1.3 cm. cell path in both experiments). The greater increased sensitivity of the Beckman B as compared to the Coleman is illustrated.

6. Curve (4) and Curve (3) were obtained by means of the Beckman B and illustrate the slight decrease of maximum absorbance occurring on standing. The measurements plotted in Curve (4) were taken one day later than those shown in (3).

7. Two other effects which were observed generally in colorimetric determinations using the Beckman DU are illustrated by Curve (5). Inefficient extraction of "porphyroxine-meconidine" or low "porphyroxine-meconidine" content result in weakly coloured red solutions. In spite of low concentrations of red material the sharp peak with only a slight shift in wave length at which maximum absorption occurs, is observed in Curve (5).

8. It may be concluded that the narrower the measurable band width the more sensitive the instrument. Thus the most sensitive instrument is the Beckman DU and the least sensitive is the Coleman. This factor must be taken into account in establishing relative colourimetric values for "porphyroxine-meconidine" determinations.

Nomenclature and meaning of Spectrophotometric Terms Employed:

9. Although the instrumental techniques described in part 3 are well established, there is still some confusion in the literature regarding the expression of results from spectrophotometry. The terms employed in this paper conform with present usage as accepted by the United States, National Bureau of Standards (7) and (8).

10. In a recent paper Fuchs and Ullrich (5) employ the symbol $E^{1\%}_{1\,cm.}$ for expre[illegible]ng their results. However, the extinction coefficient $E^{1\%}_{1\,cm.}$ generally implies a knowledge of the concentration of the absorbing material, in this case the red substance (porphyr) formed from an undetermined amount of "porphyroxine-meconidine" alkaloid. The actual concentration of porphyr material in the solution is not known and therefore it is not possible at present to express an extinction coefficient. It is possible, however, to measure the absorbance (A) and to compare solutions on this relative basis, since a straight line relation between the amount of colour and the absorbance has been established. The differences in absorbances for similar solutions with different instruments, depending on band width, should also be taken into account.

III. Experimental Results

11. In Tables I, II, and III, Absorbances and Tintometer values are compared. The measurements were made on solutions prepared from the same opium, using a 1/16" cell for the Lovibond Tintometer readings. Only the red values are recorded although small values of blue and yellow were used along with the red when necessary to match the colour.

TABLE I: ABSORBANCES (OPTICAL DENSITIES) AND TINTOMETER VALUES FOR RED SOLUTIONS FROM OPIUMS (COLEMAN SPECTROPHOTOMETER)

Origin of Opium, Country and Province	Tintometer Reading,* Red Units	Absorbance* 1.3 cm cell	Absorbance* per Tintometer Unit, 1.3 cm.cell	Absorbance* per Tintometer Unit, 1 cm cell
India				
Jaora State	10.3	0.432	0.0420	0.0323
Tonk State	6.0	0.222	0.0369	0.0284
Kotah State	17.5	0.729	0.0416	0.0320
Mewar State	4.1	0.149	0.0364	0.0279
Sailana State	11.0	0.422	0.0383	0.0295
An East Punjab State	13.2	0.430	0.0328	0.0252
Dewas Jr. State	7.8	0.290	0.0372	0.0286
A Punjab Hill State	22.0	0.790	0.0359	0.0296
Piploda State	7.3	0.385	0.0526	0.0406
Export 43385	5.0	0.298	0.0596	0.0458
Export 44121	2.4	0.127	0.0522	0.0402
Gwalior State	3.1	0.142	0.0457	0.0353
Silverwalnut S.F.	3.6	0.168	0.0466	0.0359
" Seattle	5.1	0.242	0.0475	0.0365
63913 Excise	6.2	0.292	0.0471	0.0362
Seizure of Stand.	5.4	0.258	0.0478	0.0367
Afghanistan				
Export 63909	5.1	0.231	0.0453	0.0349
Turkey				
Usak No. 1	1.0	0.060	0.060	0.0462
Usak No. 2	5.1	0.198	0.039	0.0301
Corum	0.7	0.028	0.040	0.0309
Yugoslavia, Export				
Yugoslavia 63914	3.7	0.178	0.0483	0.0371
Yugoslavia 44125	3.6	0.158	0.0438	0.0338
Yugoslavia 63915	2.0	0.094	0.0470	0.0362
Iran, Export				
Iranian 63916	2.2	0.100	0.0454	0.0349

* NOTE: The Tintometer readings were obtained with half the depth of cell used by the United Nations Secretariat, and therefore must be multiplied by two if direct comparison with the U.N. values is desired. (Concerning low readings, see paragraph 12). The Absorbances were measured on solutions equivalent to 0.6 per cent opium, not 1 per cent as used by Fuchs and Ullrich.

TABLE II. ABSORBANCES (OPTICAL DENSITIES) AND TINTOMETER VALUES FOR RED SOLUTIONS FROM OPIUMS (BECKMAN B SPECTROPHOTOMETER)

Country of Origin of Opium	Tintometer Reading* Red Units	Absorbance* 1 cm cell	Absorbance* per Tintometer Unit, 1 cm cell
India			
United Provinces (Exp. 1)	17.3	0.660	0.038
(Exp. 5)	23.0	0.750	0.033
Gwalior State	12.0	0.490	0.040
Indore State	10.2	0.404	0.040
Ratlam State	13.0	0.496	0.038
Jaora State	15.1	0.611	0.041
Sita Mau State	21.7	0.830	0.038
Tonk State	10.0	0.390	0.039
Partabgarh State	15.3	0.635	0.042
Kotah State	27.2	1.049	0.039
Sailana State (Exp. 3)	14.4	0.523	0.036
(Exp. 5)	20.0	0.760	0.038
An East Punjab State	22.0	0.742	0.034
Dewas Jr. State	13.2	0.513	0.039
Piploda State	14.4	0.530	0.038
Export 43385	12.0	0.429	0.036
Export 44121	16.0	0.650	0.041
Gwalio Biscuit Opium	3.9	0.140	0.036
Silverwalnut S.F.	5.7	0.222	0.039
Silverwalnut Seattle	13.1	0.451	0.035
Excise 63913	13.2	0.450	0.034
Seizure of Standardized	11.0	0.413	0.037
Afghanistan			
Afghanistan 63909	6.1	0.240	0.039
Afghanistan 63913	4.0	0.160	0.040
Turkey			
Isparta	3.2	0.146	0.046
Afyon (presumed)	5.7	0.211	0.039
Sandikli	2.1	0.075	0.036
Malatya	4.2	0.165	0.039
Sinav	4.5	0.196	0.044
Export 44123	4.3	0.178	0.041
Export 44124	5.2	0.214	0.041
Export 63911	4.9	0.209	0.043

(This table continued on next page)

TABLE II (cont'd)

Country of Origin of Opium	Tintometer Reading* Red Units	Absorbance * 1 cm cell	Absortance * per Tinto-meter Unit, 1 cm cell
Iran			
Export 63916	3.2	0.135	0.042
Lorestan	3.2	0.126	0.039
Isfahan	1.5	0.080	0.053
Kermanshah	0.8	0.040	0.050
Malayer (Exp. 1)	3.5	0.142	0.041
(Exp. 2)	4.0	0.145	0.036
Kerman	3.9	0.139	0.036
Khorassan	1.1	0.047	0.043
Export 63409	2.3	0.100	0.044
Stick opium, green label	3.8	0.154	0.041
Stick opium, red label	1.3	0.054	0.042
Japan 63426	29.9	1.205	0.040
(Singapore)	6.6	0.292	0.044
Mongolia 63424	4.4	0.165	0.038
Manchuria 63423	4.8	0.202	0.042
Korea	7.6	0.328	0.043

* NOTE: The Tintometer readings were obtained with half the depth of cell used by the United Nations Secretariat, and therefore must be multiplied by two if direct comparison with the U.N. values is desired.

The Absorbances were measured on solutions equivalent to 0.6 per cent opium, not 1 per cent as used by Fuchs and Ullrich.

TABLE III ABSORBANCES (OPTICAL DENSITIES) AND TINTOMETER VALUES FOR RED SOLUTIONS FROM OPIUMS (BECKMAN DU SPECTROPHOTOMETER)

Sample No. U.N.	Origin of Opium	Tintometer Reading* Red Units	Absorbance* 1 cm cell	Absorbance* per Tintometer Unit, 1 cm cell
1.	Turkey Aydin A	9.2	0.384	0.0417
		7.7	0.370	0.0480
2.	" Afyon	9.7	0.398	0.0410
		8.0	0.389	0.0486
3.	" Çorum	4.8	0.221	0.460
		4.4	0.208	0.0473
4.	" Çal B	2.6	0.127	0.0488
		2.1	0.128	0.0610
5.	" Usak A	3.1	0.136	0.516
		3.1	0.155	0.0500
6.	" Nallihan A	11.1	0.470	0.0423
		10.4	0.490	0.0471
7.	" Merzifon B	3.8	0.156	0.0411
		3.2	0.154	0.0481
8.	" Burdur	5.6	0.238	0.0425
		5.1	0.230	0.0451
9.	" Kula A	9.1	0.373	0.0410
		8.7	0.390	0.0448
10.	" Sandikli	6.2	0.267	0.0431
		5.4	0.255	0.0472
11.	" Aksehir A	5.3	0.216	0.0408
		3.7	0.194	0.0524
12.	" Zile	13.8	0.569	0.0412
		13.0	0.570	0.0439
13.	" Isparta A	6.2	0.240	0.0387
		4.5	0.226	0.0502
14.	" Malatya	16.4	0.624	0.0381
		12.0	0.560	0.0467
15.	" Export	5.7	0.244	0.0428
		4.1	0.205	0.0500

(This table continued on next page)

TABLE III (cont'd)

Sample No. U.N.	Origin of Opium	Tintometer Reading* Red Units	Absorbance* 1 cm cell	Absorbance* per tintometer Unit, 1 cm cell
16.	Korea No. 1	1.1	0.058	0.0527
		0.6	0.044	0.0733
17.	Korea No. 2	4.4	0.188	0.0427
		3.1	0.158	0.0510
24.	Yugoslavia	4.5	0.186	0.0413
		3.8	0.178	0.0468
25.	Greece	4.5	0.194	0.0431
		3.3	0.159	0.0482
26.	Indochina (Laos) (Luang Prabang)	4.3	0.210	0.0488
		3.5	0.175	0.0500
27.	Indochina (Laos) (Xieng-Khouang)	5.2	0.261	0.0502
		4.4	0.210	0.0477
28.	Indochina (Vietnam) (Laokay)	7.1	0.329	0.0463
		6.5	0.263	0.0405
34.	India (Uttar Pradesh)	12.2	0.578	0.0478
		11.5	0.520	0.0452
35.	India (Malwa) (Madhya Bharat)	11.0	0.530	0.0482
		10.3	0.477	0.0463
36.	India (Excise opium)	10.0	0.484	0.0484
		10.4	0.452	0.0435
37.	China (Taiwan)	3.6	0.203	0.0564
		4.0	0.193	0.0483

* NOTE: The Tintometer readings were obtained with half the depth of cell used by the United Nations Secretariat, and therefore must be multiplied by two if direct comparison with the U.N. values is desired.

The Absorbances were measured on solutions equivalent to 0.6 per cent opium, not 1 per cent as used by Fuchs and Ullrich.

The Tables list the absorbances observed using three different instruments; Table I, Coleman; Table II, Beckman B; Table III, Beckman DU. The observed absorbances for the Coleman (Table I) were obtained using a 1.3 cm. cell and are expressed in the last column as absorbances (A) per Tintometer unit (L) for a 1 cm. cell to correspond with the data in other Tables, as follows:

$$\frac{A}{L} \times \frac{1}{1.3} = \text{A/Tintometer Unit/1 cm light path.}$$

For example, for India, Jacra State, A/Tintometer Unit/1 cm =

$\frac{0.432}{10.3} \times \frac{1}{1.3} = 0.0323$, where A = absorbance, L = Tintometer Unit.

12. If the Tintometer values are compared, it will be noted that those in Table I are much lower than those in Table II, for the same samples. The values in Table I are the result of early experiments in extracting the "porphyroxine-medonidine", and are too low. However, this does not affect the relation between the Tintometer values and the Absorbances, since the latter were obtained on dilutions of these same solutions, as described in paragraph 2. These early results have therefore been used to determine the relation between Tintometer values and Absorbances for the Coleman instrument.

13. The average absorbances per Tintometer unit were obtained from Tables I, II, and III.

Table No.	Instrument	Average Absorbance per 1 cm per Tintometer Unit
III	Beckman DU	0.04688
II	Beckman B	0.03976
I	Coleman	0.03428

Concentration of opium, 0.6 per cent.

Comparison of Absorbances/Tintometer Unit with Results of Fuchs and Ullrich (5)

14. Our Tintometer results for direct comparison with those of the United Nations Secretariat (17) (18) and Fuchs and Ullrich (9) should be multiplied by two. The relationship, Absorbance per Tintometer unit, based on a 1% concentration with respect to opium as used by Fuchs and Ullrich (who compared their absorbances with the United Nations Tintometer values determined in New York), may be calculated using the Beckman DU average absorbance value, Table III, as follows: $\frac{0.04688}{6} \times \frac{10}{2} = 0.03906$. The average absorbance

per Tintometer unit for 1.0 per cent opium solution as measured by the Beckman DU is therefore 0.03906. It should be pointed out that our spectral maxima were measured at a wave length 511 mμ, whereas Fuchs and Ullrich (9) made their measurement at 520 mμ. Furthermore, they did not have direct comparisons with their own Tintometer values, as we did.

15. The comparison of values on the basis of 1 per cent opium equivalent, is as follows:

Instrument	Observed Absorbances per Tintometer Unit	
	at 511 mμ	Fuchs and Ullrich
Beckman DU	0.03906	0.0286 at 520 mμ
Beckman B	0.03313	--
Coleman	0.02856	--
Pulfrich	--	0.0253 at 530 mμ

Stability of the Red Colour in Solution

16. An important factor to be determined in any colourimetric method is the stability of the colour used for spectrophotometry. Analysis of the spectral curves (Fig. 1 and 2) of the red coloured solutions showed three maxima corresponding to absorption in the near ultraviolet at 285 mμ (Fig. 1) and 380 mμ (Fig. 2) and the middle visible region at 510 to 520 mμ (green) (Fig. 2). Table IV illustrates the measurements of absorbances on three solutions subjected to different conditions over a period of time; after heating, standing at room temperature in the dark, and exposed to daylight. The absorption maxima shift and the absorbances increase or decrease by several units depending on conditions, such as, temperature, light, "pH" and type of ions present in solution. Not all these factors were examined; however, it has been established that the porphyr colour is fairly stable to temperature and light changes. The solution used for these experiments was prepared from samples of Indian opium No. 19 (Gwalior State, Biscuit). The measurements were made in the usual way spectrophotometrically at timed intervals.

17. The coloured solutions are remarkably stable in the dark and daylight at room temperature, and also at elevated temperatures. They are eminently

suitable for colourimetric determinations. The peak at 380 mμ (Fig. 2) may represent either an absorption of the porphyr molecule, or of a transformation product from the porphyr molecule. The latter is probably the case, since it is observed that as the maximum at 510 mμ decreases in intensity with temperature or by other means, the maximum at 380 mμ increases. This also suggests the formation of a new product from the porphyr compound. Regardless of the meaning or interpretation of these results they do illustrate the important fact that the red coloured solutions are sufficiently stable for establishing a spectrophotometric method of analysis.

TABLE IV

COLOR STABILITY OF PORPHYR HYDROCHLORIDE SOLUTIONS FROM INDIAN OPIUMS AT VARIOUS TEMPERATURES IN DAYLIGHT AND DARK

Sample No.	Wave Length, mμ	Absorbance at various Times, Hours				Experimental Conditions
18		1	8	16	69	Hours
	390	0.080	0.079	--	0.090	) 80° C.
	510	0.127	0.122	0.119	0.108	) Daylight
19		1	7	15	65	Hours
	380	0.140	0.138	0.138	0.170	25° C.
	510	0.142	0.138	0.137	0.128	Daylight
20		1	10	--	67	Hours
	380	0.140	0.131	--	0.140	25° C.
	510	0.168	0.168	--	0.160	Dark

Comparison of Tintometer and Spectrophotometric Data:

18. By means of the Tintometer coloured solutions were matched by mixing light from three properly chosen primaries, red, yellow, and blue. Tintometer readings thus obtained for each sample of opium can be related to the spectrophotometric curve (Figures 2 and 3) in two ways. First the relationship can be established by means of tristimulus values X, Y, and Z. It is possible to calculate these by means of tables (11, 12), a set of tristimulus values corresponding to each wave length of a spectrophotometric curve, (e.g. Figure 2) at 5 mμ intervals. A spectrophotometric analysis of the Lovibond colour system was made by Gibson and Harris (15). Tintometer Ltd., makers of the Lovibond glasses have computed from the published spectrophotometric measurements the chromaticity co-ordinates x, y of all the colours of the Lovibond system (16). The "Rothamsted Obdurator Vane" enables the operator to convert directly from Lovibond to C.E.I values (22). The fundamental principles involved in such calculations have been described elsewhere (13, 17).

19. A second method of relating spectrophotometric absorption data with colorimetric data is to establish the relationship by plotting the absorbance at a chosen wave length against the Tintometer scale readings. The results are scattered about the solid straight line shown in Figure 4. The straight line was obtained using the Beckman data shown in Table III, plotted against the Tintometer readings on the same samples. There appears to be a wider scattering of the points at higher concentration of porphyr hydrochloride. It should be noted that the line shown in Figure 4 represents a correlation between the transmitted red colour(observed) and the absorbed (green) colourof light passed through the red coloured solutions. The dotted line (Figure 4) represents the "best-fit" straight line calculated by Mr. T. Kelly of this laboratory from the data in Table III by the method of least squares. The dotted line (calculated) in Figure 4 falls slightly below the solid line fitted by eye. The fitted line also intercepts the (A) absorbance axis, whereas the solid line passes through the origin. The equations of the "best-fit" line are

$$A = 0.02264\ t\ 0.04168\ T$$

or $$T = -0.35795\ t\ 23.3585\ A$$

depending on whether Absorbance (A) is expressed in terms of Tintometer (T) values or vice versa.

20. The data from Dr. Fuchs' paper and the results in Tables I, II, and III were submitted for calculation of a statistical correlation co-efficient to Mr. T. Kelly, Biometrics Section of this laboratory. The results of the calculations are shown in Table V. The high correlation co-efficients, greater than 0.9 in all sets of data (maximum = 1), show that the linear relationship between Lovibond and Absorbance values is significant and is uniform.

TABLE V. CALCULATION OF CORRELATION CO-EFFICIENTS FOR LOVIBOND-ABSORBANCE VALUES

Instrument	Set of Data	No. of Observations N	Correlation Co-efficient r	Regression Line Parameters	
				Slope b	Intercept a
Coleman	Table I	34	.989	.03819	.02219
Beckman	Table II	48	.994	.03719	.01162
Beckman DU	Table III	52	.987	.04168	.02264
Pulfrich	16 samples	16	.997	.02583	.01108
Pulfrich	10 "	11	.961	.01681	-.3044
(data left out of consideration for final relation)					
Pulfrich	All Data	27	.956	.01998	- 3.4264

Conclusions:

21. The red coloured solutions obtained have three absorption maxima, at 285 mμ, 380 mμ, and 510-520 mμ, but only the last one is certainly due to the porphyr hydrochloride.

22. Porphyr hydrochloride concentration can be estimated at 510-520 mμ. The ultraviolet peaks appear to represent two other compounds which could be estimated simultaneously.

23. A relation between the Absorbance and the Tintometer reading was established for the Beckman DU, Beckman B, and Coleman spectrophotometers. These are 0.0391, 0.0331 and 0.0286 absorbance per Tintometer unit for the Beckman DU, B, and the Coleman respectively. The last value corresponds fairly well with a preliminary value obtained by the United Nations Secretariat (19) (about 0.030). (The solution representing the colour developed from 1 gm opium and in 100 ml solution in each case.)

24. The stability of the porphyr hydrochloride solutions has been studied, and only minor changes over a long period of time were observed. The solutions are remarkably stable in colour.

25. A high correlation between Absorbance and Lovibond values was obtained. The correlation co-efficient for our data is 0.98.

REFERENCES

1. "Chemical Spectroscopy" by Wallace R. Brode, Second Edition, John Wiley & Sons Inc., 1943, P. 1, P. 4.

2. "Practical Spectroscopy" by Harrison Geo.; Lord, Richard; and Loofburrow, John. Prentice and Hall Inc. 1948.

3. "La Colorimetric ou Photometric Ses avantage et ses inconvenients" par Georges Dufrasne, "Universite Libre de Bruxelles" Chimie Analytique, 1950, 55-60.

4. "Ultraviolet Spectra of Aromatic Compounds" by Robert A. Friedel and Milton Orchin. John Wiley and Sons Inc., New York, Chapman and Hall Ltd., London, 1951, pp. 1, 35.

5. Twyman and Lothian, "Absorption Spectrophotometry", Hilger and Watts Ltd., London, 1949.

6. Beckman Bulletin 206-B, National Technical Laboratories, South Pasadena, California; also 91-G (Beckman Quartz Spectrophotometer).

7. Letter Circular LC.-857 (1947), National Bureau of Standards, Washington, U.S.A.

8. Joint Committee on Nomenclature of A.S.T.M. Committee E-2 on Emission Spectrosccpy and the Society for Applied Spectroscopy, Report No. 4, (1950).

9. Fuchs, L. and Ullrich, W., Document ST/SOA/SER.K/10, "The Colorimetric Determination of 'Porphyroxine-Meconidine'; Communication on Experiments to find a Relation between 'Red Lovibond Units' and Absorption Intensity Values of Red 'Porphyr' Solution."

10. "Tintometer Publications on Colour and Visual Measurement of Colour." (Collection of Reprints) - Published by The Tintometer Ltd., Milford, Salisbury, Eng.

11. "Colorimetry", National Bureau of Standards Circular 478.

12. "Color in Science and Industry", D.B. Judd, 1952. (John Wiley and Son, New York).

13. "Spectrophotometry for Chemists" by Robert S. Casey, W.A. Sheaffer Pen Co., Fort Madison, Iowa. Journal of Chemical Education 24, 446, 1947.

14. Mellon, M.G., "Analytical Absorption Spectroscopy", John Wiley & Sons Inc., New York, 1950, pp. 558, 559.

15. Gibson, K.S. and Harris, F.K., and Priest, I.G., Natl. Bur. Standards, Sc. Paper 547, 1917.

16. Scoffield, R.K., Sci. Instrument 16, 74, (1939).

17. United Nations Secretariat, "The Comparative Determination of 'Porphyroxine-Meconidine'." E/CN.7/195.

18. United Nations Secretariat, " 'Porphyroxine-Meconidine' in relation to the origin of opium." ST/SOA/SER.K/4.

19. Communication from C.C. Fulton as co-ordinator of the international opium research, 25 October 1952.

20. Farmilo, C.G. and Kennett, P.M.L., "Further Data on 'Porphyroxine-Meconidine' ", Document E/CN.7/207, 19 October 1950.

21. Hirt, R.C., "Sources of Information on Ultraviolet Absorption Spectrophotometry, Journal of Chemical Education, Vol. 29, 301, (1952).

22. The Tintometer Ltd. (Milford, Salisbury, Eng.) "Colorimetry", Part II, The Lovibond-Schofield System, p. 12. 1950.

23. Ashley, S.E.Q. "Progress Report of Committee on Nomenclature", Division of Analytical Chemistry, 1952. Analytical Chemistry Journal, 24, 1348 (1952).

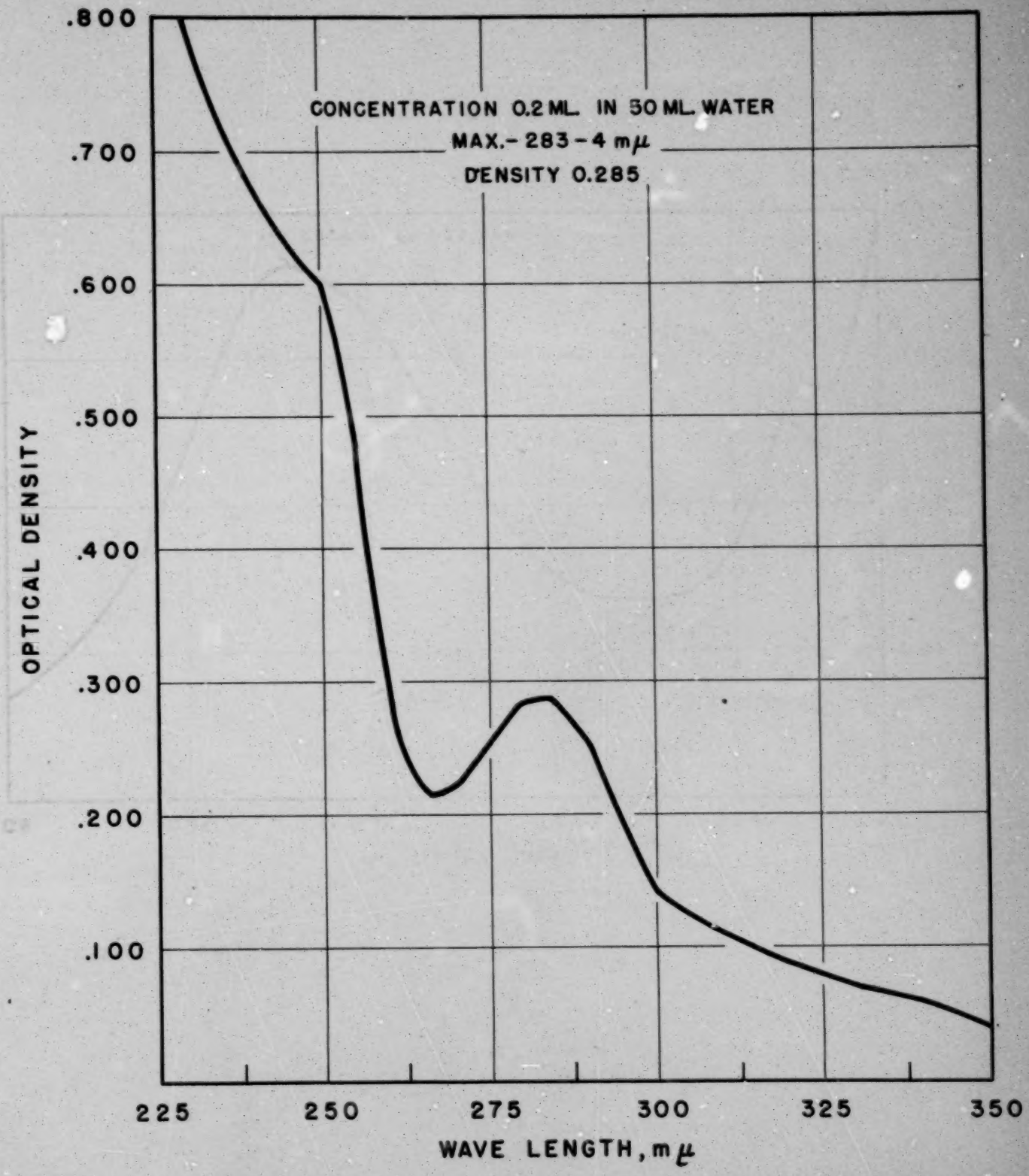

Fig. 1. ABSORBTION SPECTRUM (ULTRA VIOLET) OF SUBSTANCE PRESENT IN "PORPHYROXINE-'NSCONIDINE" EXTRACTS

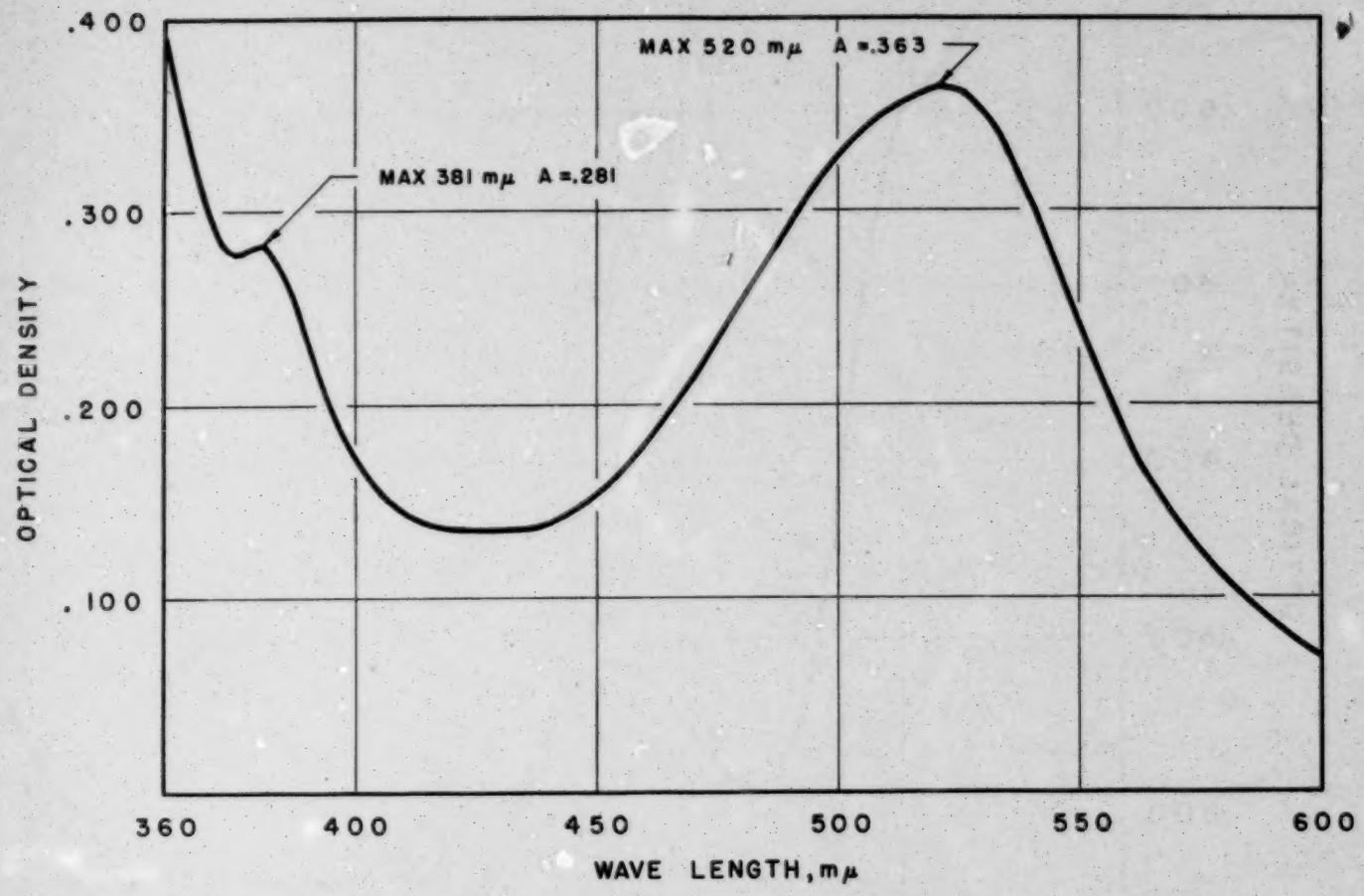

Fig. 2. ABSORBTION SPECTRUM (ULTRA VIOLET AND VISIBLE) OF PORPHYR HCL SOLUTIONS FROM OPIUM

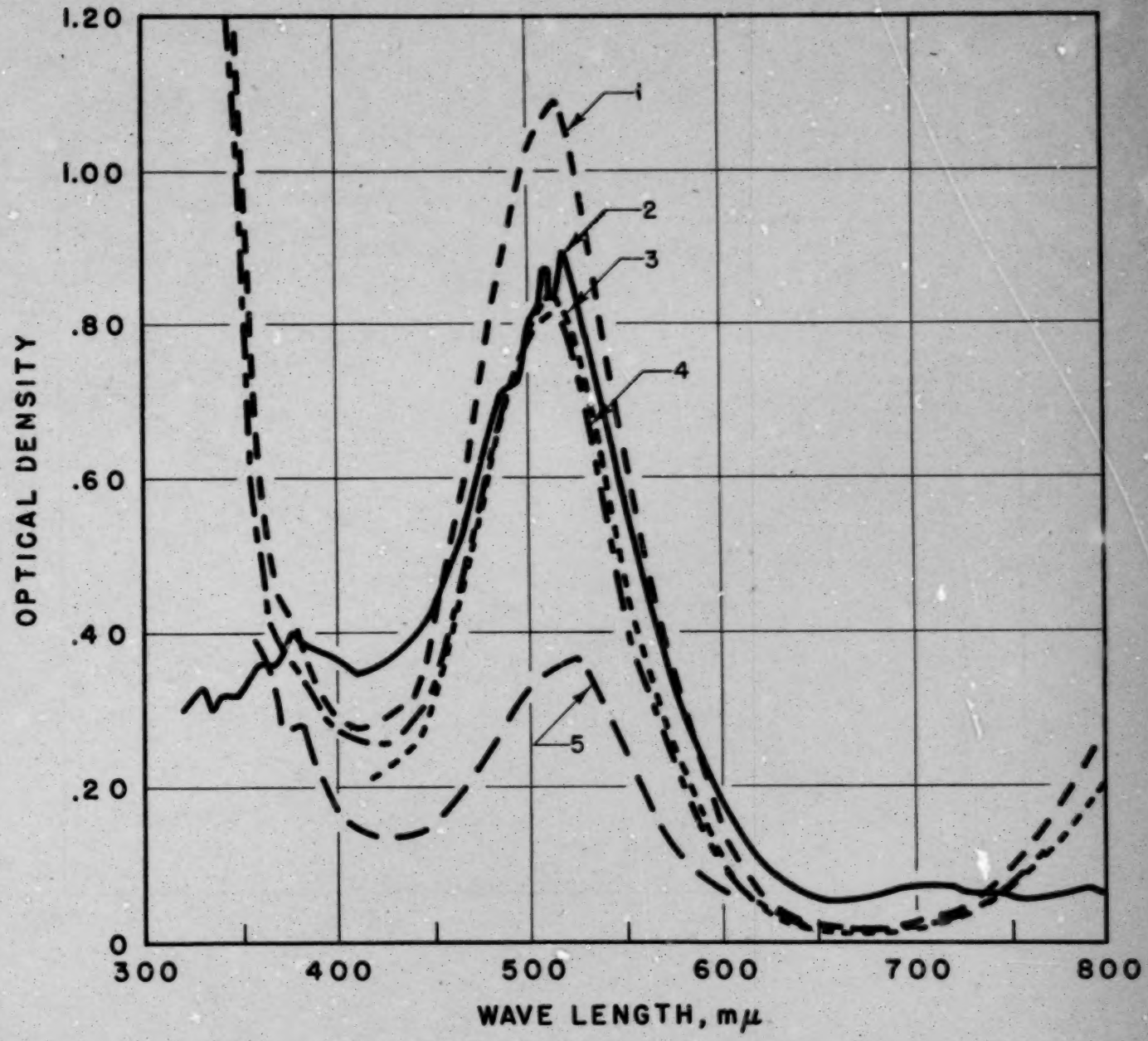

Fig. 3 COMPARISON OF ABSORPTION SPECTRA OF PORPHYR HCL SOLUTIONS MEASURED WITH THREE SPECTROPHOTOMETERS

_ _ _ _ _ CURVE 1 - BECKMAN B USING 1.3 CM CELL)
)
_____ CURVE 2 - COLEMAN USING 1.3 CM CELL) SAME PORPHYR CONCENTRATION
)
. . . . . CURVE 3 - BECKMAN B USING 1.0 CM CELL)

_ _ _ _ _ CURVE 4 - BECKMAN B USING 1.0 CM CELL (Decrease of absorbance on standing)

_ _ _ . _ CURVE 5 - LOW PORPHYR CONCENTRATION (BECKMAN DU)

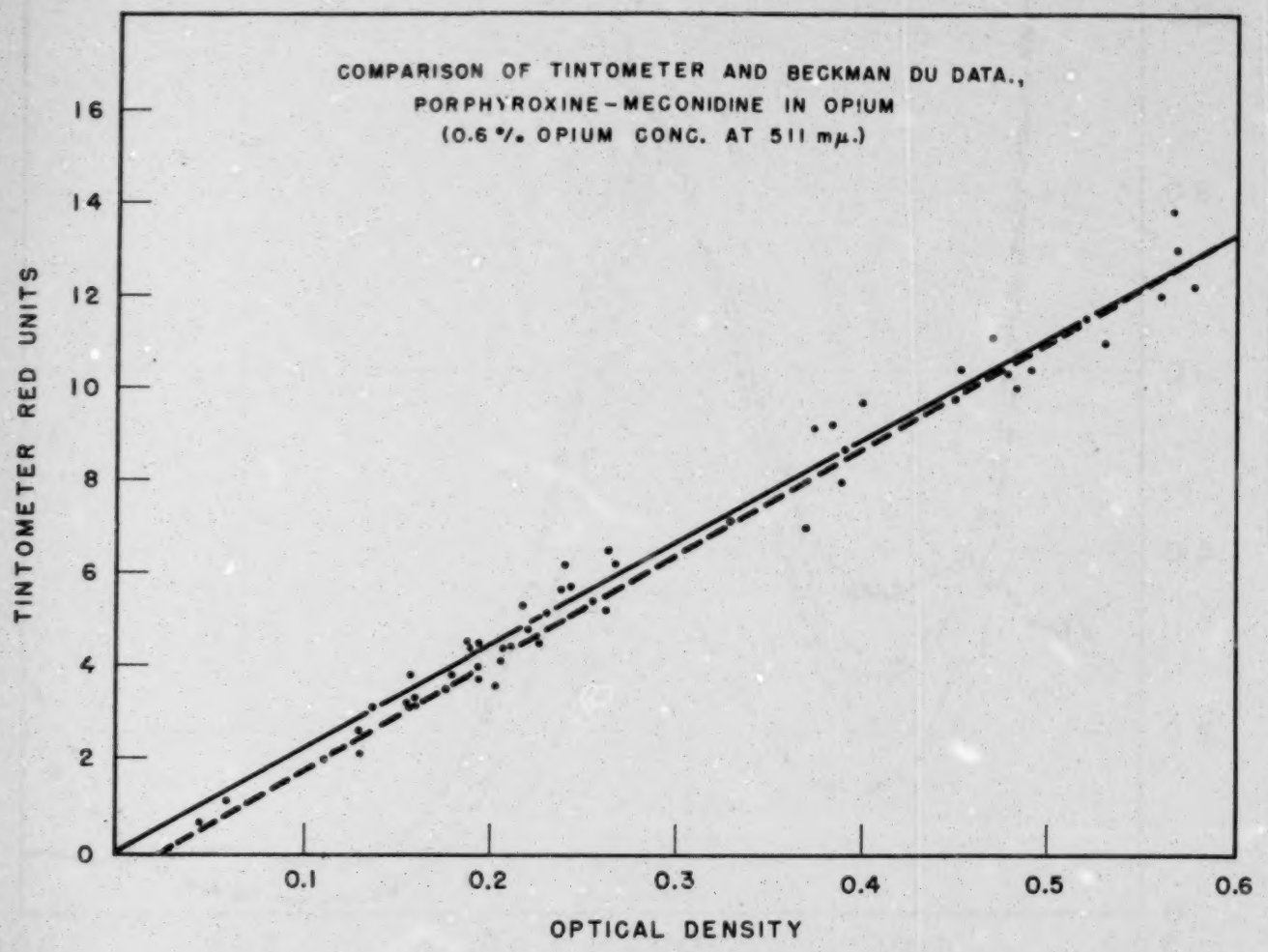

Fig.4 RELATIONSHIP BETWEEN ABSORBANCE (OPTICAL DENSITY) MEASURED AT 511 mμ (GREEN) AND (LOVIBOND) TINTOMETER VALUES (RED COLOR ONLY)